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A Green's function estimation of lattice relaxation for substitutional defects in metals over the entire composition range

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Abstract In this paper, we present a method to calculate nearest neighbour (n n) separation as a function of concentration of substitutional defects in binary metallic alloys The model is based on a Green's Function technique to calculate n n relaxation in conjunction with Huang's idea for extension to high concentration range. Morse potential function is used to represent two-body potential between the atoms The potential parameters for the unlike interactions are calculated using simple interpolation formulae Distant neighbour relaxation is calculated by invoking a continuum approximation Initial application of the model to (K-Cs) alloy shows encouraging results

Keywords Lattice relaxation, substitutional alloy, Green's function

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1. Introduction

In studies of point defects, lattice relaxation plays an important role. Earlier, we had developed a consistent semi-discrete approach for the determination of the lattice relaxation and applied the same for the studies of substitutional defects in alkali halide solid solutions [1] and obtained good agreement with experimental results. Besides the above method, there is another more powerful and theoretically more rigorous method based on a Green's function to determine lattice relaxation. The Green's function approach has been discussed in detail by Caldwell and Klein [2] and by Tewary [3]. In a previous paper [4], we had employed the Green's function method to study the variation of nearest neighbour (n.n.) separation with concentration of defects in alkali halide solid solutions and have got encouraging results. In this paper, we try the above approach to estimate lattice relaxation and hence to study the variation of n. n. separation with concentration of defects in (*K -Cs*) alloy (where *K* is substituted by *Cs* atom) over the entire concentration range of substitutional atoms.

In studies of point defects, it is usual to divide the crystal into two regions. Region I consists of the immediate neighbourhood of the point defect, and this region is treated in

detail, atomistically. The remaining portion of the crystal is the region II. Using the continuum approximation for the region II, one puts the relaxation of an ion at a distance r from the defect as K/r^2, where K is a constant which we call the defect strength constant. For the region I, relaxation, $u_{n\,n}$, of nearest neighbour to defect is written as $u_{n\,n} = \xi r_1$, where r_1 is the nearest neighbour distance of the host crystal and ξ is a parameter determined by the Green's function discussed in the next section. Several different procedures for the determination of the constant K exist in the literature [5-7]. In this paper, we follow the method suggested by Datta Roy (Paul) and Sengupta [4]. The details of the procedure of determination of K is also discussed in the next section.

In finding the static Green's function we have made use of Born's idea of replacing $\omega^2(q, j)$ by an average Einstein frequency $<\omega^2>$. This approximation seems to be justified in view of the fact, pointed out by Bullough and Tewary [8] that the static Green's function is not very sensitive to the details of the phonon dispersion.

For the high concentration region we have extended the Huang's [9] idea of a mean lattice plus fluctuations propagating through the continuum. This continuum picture is applicable for distant neighbour relaxations in the Green's function method also [3]. It may be mentioned that Tewary solved for the change in the Green's function matrix for point defects and obtained as asymptotic behaviour for the lattice distortion. He found that for a substitutional defect, the relaxation $u(l)$ for large l in a cubic lattice is proportional to $(1/l^2)$ which is the same as predicted by the continuum theory.

Extension of Huang's idea to high concentration of defects gives a very simple model which correctly predicts the n.n. separation for (K-Cs) substitutional solid solution over the entire composition range. Here we compare the deviations of the calculated values of the nearest neighbour separations from those predicted by Vegard's [10] law with the corresponding deviations from the experimental values. The two deviations agree within reasonable limits. The simplicity of the model is appealing considering the agreement with experiment and huge reduction of computational time and effort.

2. Theory

For a monatomic crystal, the relaxation $\boldsymbol{U}\begin{pmatrix} l \\ \alpha \end{pmatrix}$ of an ion in the 1-th cell along the $\alpha\,(=x, y, z)$ direction is given by

$$\boldsymbol{U}\begin{pmatrix} l \\ \alpha \end{pmatrix} = \sum_{l',\beta} G\begin{pmatrix} l & l' \\ \alpha & \beta \end{pmatrix} \boldsymbol{F}\begin{pmatrix} l' \\ \beta \end{pmatrix}, \tag{1}$$

where the lattice static Green's function $G\begin{pmatrix} l & l' \\ \alpha & \beta \end{pmatrix}$ is defined by

$$G\begin{pmatrix} l & l' \\ \alpha & \beta \end{pmatrix} = m\Phi^{-1}\begin{pmatrix} l & l' \\ \alpha & \beta \end{pmatrix} = (1/N)\sum_{q,j}\left[\boldsymbol{b}(q,\alpha,j)\,\boldsymbol{b}^*(q,\beta,j)\exp\left[iq.(r_l - r_{l'})\right]/\omega^2(q,j)\right] \tag{2}$$

where m is the mass of an ion of the pure crystal, Φ is a square $(3N \times 3N)$ force constant matrix of the pure crystal, N, the number of cells in the crystal, $\boldsymbol{b}(q, \alpha, j)$, the eigenvectors and $\omega(q, j)$, the eigenfrequencies and $j = 1, 3$. $\boldsymbol{F}\begin{pmatrix} l' \\ \beta \end{pmatrix}$ in eq. (1) is the additional force experienced by

an A (host) ion in the l' cell along the β ($= x, y, z$) direction due to the substitution by a foreign B (defect) ion at the origin. From eqs. (1) and (2), we can find the displacement $\boldsymbol{U}\begin{pmatrix} l \\ \alpha \end{pmatrix}$ of an ion of the pure crystal provided the phonon spectrum of the perfect lattice is known. In the present paper, we have replaced $\omega^2(q, j)$ by an average Einstein frequency defined by

$$<\omega^2> = (1/3N)\,\Sigma_{q,j}\,\omega^2(q,j). \tag{3}$$

We have used Morse potential for the purpose of calculations of $<\omega^2>$ and $\boldsymbol{F}\begin{pmatrix} l' \\ \beta \end{pmatrix}$. For a two-body central potential $\phi(r_{ij})$

$$<\omega^2> = 1/(3m)\,\Sigma_{\alpha,l',\beta}\left[(r_{ij\alpha}\, r_{ij\beta}/r_{ij}^{\,2})\,\phi''(r_{ij}) + (\delta_{\alpha\beta}/r_{ij} - r_{ij\alpha}\, r_{ij\beta}/r_{ij}^{\,3})\,\phi'(r_{ij})\right]. \tag{4}$$

For a *b.c.c.* crystal and interaction upto the next nearest neighbour (n.n.n), we can write

$$<\omega^2> = (2/m)\left[\frac{4}{3}\,\phi_1''(r_1) + \frac{8}{3\sqrt{3}r_0}\,\phi_1'(r_1) + \phi_2''(r_2) + \frac{\phi_2'(r_2)}{r_0}\right], \tag{5}$$

where $2r_0$ is the lattice parameter, r_1 and r_2 are, respectively, the nearest neighbour (*n.n*) and second nearest neighbour distances. Relaxation of the A ion at the *n.n.* site of the defect B ion at the origin is

$$\boldsymbol{u}\begin{pmatrix} l=n,n \\ \alpha \end{pmatrix} = \frac{\boldsymbol{F}\begin{pmatrix} l=n,n \\ \alpha \end{pmatrix}}{m<\omega^2>} \tag{6}$$

2.1. Potential parameters for like and unlike atomic interactions :

The Morse potential function is usually written in the form

$$\phi(r_{ij}) = D\left[\exp\left(-2\alpha(r_{ij} - r_0)\right) - 2\exp\left(-\alpha(r_{ij} - r_0)\right)\right], \tag{7}$$

where D, α and r_0 are potential parameters. We shall, however, use a more convenient but equivalent form given by

$$\phi(r_{ij}) = \tilde{D}\left[\exp\left(-2\tilde{\alpha}(r_{ij} - \sigma)\right) - \exp\left(-\tilde{\alpha}(r_{ij} - \sigma)\right)\right], \tag{8}$$

where

$$\tilde{D} = 4D,\ \tilde{\alpha} = \alpha \text{ and } \sigma = r_0 - \frac{ln2}{\alpha}. \tag{9}$$

The cohesive energy per particle is given by

$$E = \frac{1}{2}\,\Sigma'_{ij}\,\phi(r_{ij}). \tag{10}$$

Considering interactions upto the second neighbour and the potential given by eq. (7) or (8) we get

$$E = \frac{n_1}{2}\phi_1(r_1) + \frac{n_2}{2}\phi_2(r_2). \tag{11}$$

where n_1 and n_2 are the number of equivalent sites for the nearest neighbours (*n.n*) and next nearest neighbours (*n.n.n*) and r_1 and r_2 are the respective separations. $n_1 = 8$, $n_2 = 6$ and $r_2 = \frac{2}{\sqrt{3}} r_1$ for a BCC crystal. We now have the equilibrium condition

$$\frac{\partial E}{\partial r_1} = 0, \tag{12}$$

where $\tilde{r}_1$ is the harmonic value of the nearest neighbour separation. The expression for the harmonic bulk modulus can be written as

$$\eta = V\frac{d^2E}{dV^2} \tag{13}$$

where V is the volume per atom. $V = \frac{4}{3\sqrt{3}} r_1^3$ for a BCC crystal. Eqs. (11), (12) and (13) can be used to determine the potential parameters for pure metals, using the experimental values of the cohesive energy corrected for zero point effect, the harmonic values of the lattice parameter and bulk modulus. These parameters along with the data used for their evaluation are listed in Table 1. The potential parameters for unlike interactions have been determined following the combination rules adopted for unlike molecular interactions in gas pairs on the basis of the Morse potential function [11]. The combination rules for unlike interactions may be summarized in the following way. If the potential parameters for A-type atoms are D_A, α_A and σ_A and D_B, α_B and σ_B are the corresponding parameters for the B-type atoms, then the parameters for the AB interaction are determined from the interpolation formulae [11],

$$D_{AB} = \sqrt{(D_A D_B)}, \tag{14}$$

$$\alpha_{AB} = 0.5(\sigma_A + \sigma_B), \tag{15}$$

$$\sigma_{AB} = \sqrt{(\sigma_A \sigma_B)}. \tag{16}$$

Table 1. Parameters of the Morse potential for pure metals and data used for their evaluation The harmonic lattice parameters is denoted by d. d is calculated by using harmonic density ρ and atomic weight Cohesive energy is denoted by E. The harmonic bulk modulus is denoted by η

Metal	ρ[12] (gcm^{-3})	d (10^{-8} cm)	E[13] (10^{-12} $erg/atom$)	η[12] (10^{12} $dyne/cm^2$)	D (10^{-13} erg)	α (10^{8} cm)	r_0 ($10^{-8}cm$)
K	0.925	5.1971	1.5073	0 043	2.2800	0.6350	4.7164
Cs	2.020	6.0231	1.3247	0.025	2.0050	0.5550	5.4643

The parameter r_{0AB} is related to the parameter σ_{AB} by

$$r_{0AB} = \sigma_{AB} + \frac{ln2}{\alpha_{AB}}. \tag{17}$$

The parameters determined in this manner are listed in Table 2.

Table 2. Parameters of the Morse potential for (AB) interactions from combination rules

Alloy (A-B)	D (10^{-13} *erg*)	α (10^{8} *cm*)	r_0 (10^{-8} *cm*)
K–Cs	2.1381	0.5950	5.0740

2.2. High concentration of defects :

For high concentration of defects, we consider the final concentration to be achieved by successive addition of a single defect. For a finite concentration we do not consider the defect-defect interaction directly, but assume the crystal to be an elastic continuum where distortions due to different defect ions get superimposed in such a way that at any stage of the process the defect crystal retains its perfect lattice structure with a modified lattice parameter. To obtain this modified lattice parameter, we extend Huang's [9] idea of uniform lattice expansion for high concentration of defects. Huang considered the crystal to be an elastic continuum with radial relaxation given by $u(r) = \frac{K}{r^3} r$, where K is the defect strength constant. For a random distribution of foreign atoms in a dilute solution, Huang obtained the modified *n. n.* separation to be

$$r(\chi) = r\left(1 + \frac{4\pi K}{3V}\chi\right), \tag{18}$$

where r is the *n.n.* separation in the perfect lattice, $r(\chi)$ that at concentration χ and V is the volume per atom. Here we have dropped the subscript 1 in r for convenience.

A straightforward extension of Huang's expression to high concentration gives, in a host crystal A where a fraction χ of A ions is substituted by guest B ions, then the modified *n.n.* separation is given by the equation :

$$r_A(\chi) = r_A\left(1 + \frac{4\pi K}{3V}\chi\right), \tag{19}$$

where r_A is the *n.n.* separation of the pure A crystal. If at this stage a further defect ion B is added, then the background will have a *n.n.* separation given by eq. (19) whereas A ions which are *n.n.* to a defect B ion will receive a relaxation $u(111) = u_{nn}$, given by eq. (6). Thus, the *n.n.* separation of the further modified crystal is given by

$$r_{AB}(\chi) = r_A\left(1 + \frac{4\pi K}{3V}\chi\right) + u_{n\,n.(A)}, \tag{20}$$

where $u_{n.n.(A)}$ is the relaxation suffered by an A ion (host ion) which is a *n.n.* to a defect B ion. Now, the same concentration composition of the A-B solid solution could be reached from the

B-host crystal by replacing the $\chi' = (1-\chi)$ concentration of the A ion in the B-host crystal. The corresponding equations similar to the eqs. (19) and (20) are given by

$$r_B(\chi') = r_B\left(1+\frac{4\pi K'}{3V}\chi'\right), \tag{21}$$

$$r_{BA}(\chi') = r_B\left(1+\frac{4\pi K'}{3V}\chi'\right) + u_{nn(B)}, \tag{22}$$

where $u_{nn(B)}$ is the relaxation suffered by a B ion (host ion) nearest to a defect A ion in the modified crystal obtained from the B-crystal by substituting a fraction χ' of pure B ions by defect A ions. In the expressions for $r_{AB}(\chi)$ and $r_{BA}(\chi')$, we have taken the *n.n.* relaxation obtained from A (*i.e.* $u_{nn(A)}$) or perfect B (*i.e.* $u_{nn(B)}$) crystal data over the entire concentration range. There will be slight variation in u_{nn} if calculated with $r(\chi)$ as the host *n.n.* separation for intermediate stages. But because the order of magnitude of this variation is very small compared to $r(\chi)$, we have ignored this variation in u_{nn}

2.3. Evaluation of the defect strength constant K :

To find the defect strength constant K, we refer to the detailed discussion of Paul and Sengupta [1] and write

$$K = ku_{nn}\, r^2 \tag{23}$$

such that the factor k will determine the smooth merging of the microscopic relaxation experienced by the *n.n.* of the defect to the macroscopic strain developed in the rest of the crystal. The value of k is determined from the boundary conditions, at

$$\chi = 0,\ r_A(\chi) = r_A$$

and

$$\chi = 1,\ r_{AB}(\chi) = r_B$$

and is found for BCC structure to be equal to

$$k = -\frac{1}{3^{1/2}\pi}\left[1+\frac{\Delta r}{u_{nn}}\right], \tag{24}$$

where $\Delta r = r_A - r_B$, the difference of the *n.n.* separations of two perfect crystals.

2.4. Average nearest neighbour separation of an alloy :

The n.n. separation of the modified crystal formed when a fraction of A ions of the host A crystal are substituted by B ions is given by, using the value of k obtained from eq. (24) and eqs. (19, (23),

$$r_A(\chi) = r_v - \chi u_A \tag{25}$$

where $r_v = r_A(1-\chi) + r_B$ is the *n.n.* separation of the alloy according to Vegard's law. Here, we have dropped the subscript *n. n.* in u for convenience, u_A indicates relaxation of an A ion which

is *n.n.* to a defect *B* ion. Similarly, starting from a pure *B* crystal, the *n. n.* separation when a fraction χ' (= $1-\chi$) of *B* ions are substituted by guest *A* ions is given by

$$r_B(\chi') = r_v - \chi' u_B \,. \tag{26}$$

Finally, the *n.n.* separation for an alloy $A_{1-\chi}B_\chi$ is given by

$$< r(\chi) > = \chi r_B(\chi') + (1-\chi) r_A(\chi) = r_v - \chi(1-\chi)(u_A + u_B) \,. \tag{27}$$

3. Results and discussion

For K-Cs alloy, our calculations give $u_A = 0.1149$ and $u_B = -0.1005$ (in unit of 10^{-8} cm) (see Table 3). Using the above values, we calculate the theoretical deviation $\Delta r' = < r(\chi) > - r_v$ at different values of χ. We compare these deviations with the experimental values in Figure 1.

Table 3. Nearest neighbour relaxations for the dilute alloys

Alloy (A–B)	$u_{n.n}$ (10^{-8} cm)
K-Cs	0.1149
Cs-K	−0.1005

From the Figure 1, we note that the signs of theoretical deviations agree with those of the experimental deviations over the entire concentration range. Considering the simplicity of the

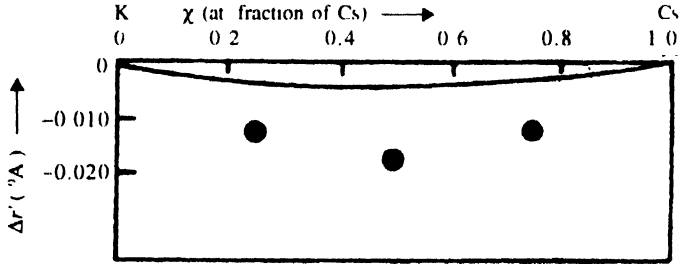

Figure 1. Plot of the deviation $\Delta r'$ (= < r (χ) > − r_v) *vs* concentration (χ). Calculated results are shown by continuous (-) curve and the experimental values [14] by Solid circles (•)

present model and the uncertainty of experimental results the above agreement is not bad, although the quantitative agreement between theoretical and experimental values is not good. Investigations with other metallic alloys are in progress and will be reported elsewhere.

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